

The structure of the Pd(1 1 0)(2 × 1)-CO surface

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Abstract

The structure of the Pd(1 1 0)(2 × 1)-CO ordered adsorption phase has been determined by scanned-energy mode photoelectron diffraction. The CO molecules are adsorbed close to short-bridge sites with alternating tilts along the close-packed ⟨1 1 0⟩ surface rows. This local geometry is consistent with that found in previous theoretical total energy calculations and an earlier X-ray photoelectron diffraction study, but is in direct contradiction to the results of an earlier quantitative low energy electron diffraction investigation. While the best-fit model structure involves some twist of the CO molecules out of the ⟨1 0 0⟩ mirror planes of the surface creating a surface phase of p1g1 symmetry, the more symmetric p2mg falls within the estimated limits of precision of the analysis. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The adsorption of CO on metal surfaces is one of the most extensively studied topics in surface science. It provides a model system of molecular adsorption which is superficially simple (although it has actually proved to be quite complex). Furthermore, an understanding the interaction of CO with such surfaces provides a starting point for

understanding quite a number of surface-induced chemical reactions (heterogeneous catalysis) such as CO oxidation of relevance to pollution control. CO is also one of only a small number of molecular adsorbates which has been subjected to investigation by quantitative structural methods. For many years vibrational spectroscopy, and notably the quantitative value of the C–O stretching frequency [1] was used as a spectral fingerprint of the local co-ordination site on the surface, but a small number of cases have shown that this is not always reliable [2–7], highlighting the need for more widespread use of truly quantitative structural methods. This is especially true because of the complex and apparently very subtle character of CO–metal bonding, with local adsorption site

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changes between different surfaces of the same element, the same face of different elements, and even as a function of coverage on a single surface. A significant number of such structures have now been solved, although the most recent survey of such data [8] only lists 12 different metal surfaces (of only seven different metals) on which such data are available.

One structural phase of adsorbed CO on fcc(110) surfaces (of Ir, Ni, Pd, Pt and Rh) which has proved of special interest is the (2×1) 1 ML coverage phase; the low energy electron diffraction (LEED) pattern in these systems shows characteristic ‘missing’ beams at normal incidence which imply that the surface space group is either $p1g1$ or $p2mg$. Lambert, who first recognised the significance of these LEED features [9], suggested that this could be understood in terms of the CO molecules along the close-packed surface $\langle 110 \rangle$ direction being alternately tilted in the perpendicular $\langle 100 \rangle$ azimuth, yielding a (2×1) periodicity of the appropriate space group from a 1 ML coverage which might otherwise be expected to show a (1×1) periodicity. Direct evidence for these tilts of the adsorbed CO were obtained quite early on, for example by angle-resolved valence band (ultraviolet) photoemission (ARUPS) on Pt(110) [10], and on Ni(110) by electron-stimulated desorption ion angular distributions (ESDIAD) [11], ARUPS [12] and X-ray photoelectron diffraction (XPD) [13]. Whether the symmetry of these surface phases is $p1g1$ or $p2mg$ is not absolutely clear; the ARUPS [12] and ESDIAD [11] data on Ni(110) certainly favour the $p2mg$ symmetry, but a small distortion of the CO molecular tilts out of the mirror plane to give $p1g1$ cannot be excluded by these measurements. The local adsorption site of the CO molecules on the surface has proved somewhat more controversial, with support for both short-bridge and atop sites, although most investigations favour the short-bridge sites. Of course, it is not necessarily the case that the same local site is occupied in this phase on all these different fcc(110) surfaces. A clear example of this variability is the case of the 0.5 ML $c(4 \times 2)$ phases formed by adsorbed CO on Ni(111), Pd(111) and Pt(111). In the case of Ni [2–5] and Pd [6] the molecules occupy threefold coordinated

hollow sites, whereas on Pt(111) a mixture of atop and bridge sites are occupied [14].

The interaction of Pd(110) with CO shows some complexities which are not seen in all the other fcc(110) surfaces. In particular [15,16], at intermediate coverages (around 0.30–0.75 ML) CO leads to a (4×2) phase which appears to be based on a (1×2) ‘missing row’ reconstruction of the Pd surface [17], but at higher coverages up to 1 ML the surface then apparently ‘unreconstructs’ to give the (2×1) $p1g1$ or $p2mg$ phase. The first quantitative structural study of this surface by LEED [18] concluded that the CO molecules occupy atop sites, but all subsequent theoretical total energy calculations favoured the short-bridge sites [19–23]. One further experimental structural study has been conducted using a novel form of XPD [24,25]. In this experiment the angular dependence of the ‘surface-shifted’ Pd $3d_{5/2}$ photoemission signal associated with the outermost Pd layer atoms was investigated to try to exploit the difference in forward scattering expected for CO in the atop or bridge sites. In fact the difference seen in the simulations for these two geometries was rather modest, but the results did appear to favour the bridge site model.

We should finally comment on the results of vibrational spectroscopy on this system. As remarked earlier, the value of the C–O stretching frequency has been used extensively in the past as a spectral ‘fingerprint’ of the coordination site, based especially on extensive early characterisation of silica-supported metal particles [26]. It was suggested that values in the range 2000–2130 cm^{-1} were characteristic of singly coordinated atop sites, those in the range 1880–2000 cm^{-1} indicated bridge sites, and lower values indicate sites of higher coordination [1]. It was on this basis that CO adsorption on Ni(111) and Pd(111) was long believed to involve bridge sites, but subsequent true structural studies showed threefold coordinated hollow sites to be occupied on both surfaces. In the case of the Pd(110)(2×1)-CO phase the observed frequency is 2004 cm^{-1} , but at low coverages the frequency is much lower (around 1890 cm^{-1}) and it was therefore generally believed that bridge sites were adsorbed [27,16], the rather high frequency at the high (1 ML) coverage being a

consequence of dynamic dipole coupling. Indeed, in the quantitative LEED investigation of the Pd(110)(2 × 1)-CO structure in which it was concluded that the adsorption was in atop sites, this case was cited [18] as another example of the failure of vibrational spectroscopy to provide incisive site assignments, especially as the Ni(110)-(2 × 1)-CO phase shows a very similar C–O stretching frequency of 1998 cm⁻¹ [28,29] but is found to involve bridge bonding [30,31].

Here we present the results of a new quantitative structure determination of the Pd(110)(2 × 1)-CO surface using C 1s scanned-energy mode photoelectron diffraction (PhD), a technique [32] which has proved very sensitive to the local geometry of adsorbed atomic and molecular species on surfaces. We find that the CO molecules are adsorbed in local bridging sites, providing final resolution of a long-standing controversy and removing this one apparent anomaly of atop adsorption from this group of fcc(110)(2 × 1)-CO structures which have been determined.

2. Experimental details

The experiments were conducted at undulator beamline 7.0.1 of the Advanced Light Source (ALS) [33] at the Lawrence Berkeley National Laboratory in California. The C 1s photoemission spectra were recorded using a Perkin–Elmer Omni IV hemispherical analyser of mean radius 137 mm fitted at a fixed angle of 60° to the incident photons. The ALS is a third-generation synchrotron radiation source and the associated undulator beamline provides substantially better spectral resolution (resolving power > 8000 [34]) than is typical of second-generation sources. For the present work this proved a significant advantage in separating the intrinsically narrow adsorbate C 1s photoemission signal from the intense but intrinsically broad substrate Pd MMN and MNN Auger peaks which overlap at certain photon energies. The Pd(110) sample, initially prepared by the usual combination of alignment with Laue X-ray diffraction, spark machining and polishing, was cleaned in situ by a combination of 1 keV Ar⁺ ion bombardment and elevated temperature (820 K)

exposures to oxygen gas (7.5×10^{-8} mbar for 5 min) followed by flashing to 910 K. The resulting surface was clean as judged by soft X-ray photoelectron spectroscopy (using the synchrotron radiation) and showed a well-ordered (1 × 1) LEED pattern. The (2 × 1)-CO surface was prepared by exposing the surface to 4×10^{-6} mbar s of CO at a sample temperature of 160 K.

The PhD technique involves the measurement of the intensity of an adsorbate core level photoemission signal as a function of photoelectron kinetic energy in a series of fixed emission directions. This emitted intensity represents a coherent sum of the directly emitted component of the photoelectron wave field and other components elastically scattered from atoms surrounding the emitter. Therefore, as the photoelectron energy, and thus wavelength, is varied, these scattering pathways switch in and out of phase leading to modulations in the measured intensity. Simulations of these modulations using different possible model structures allow the local structure around the emitter to be determined. In general for a molecular adsorbate it is possible to obtain separate PhD modulation spectra for each constituent atomic species, but in the present case the very close proximity of the O 1s and Pd 3p_{3/2} peaks meant that it was only possible to collect data using the C 1s peak. Of course, as CO bonds to surface via the C atom, PhD from this atom which is closest to the surface is most sensitive to the adsorption site. The PhD data were collected by measuring a sequence of short C 1s photoelectron energy distribution curves (EDCs) at a sequence of increasing photon energies for each emission direction. The photon energy steps were chosen to correspond to a constant size of step in the photoelectron wavevector of $\Delta k = 0.039 \text{ \AA}^{-1}$ and covered the range of k from 4.3–10.9 \AA^{-1} (kinetic energies 70.4–452.5 eV) although data at the lowest kinetic energies (below 120 eV) were not used in the subsequent analysis due to a problem experienced with the low energy performance of the electron energy analyser during our run.

Fig. 1(a) shows a typical set of such EDCs from a single PhD measurement, showing rather clearly the intense Pd Auger electron emission peaks around kinetic energies of 240, 270 and 325 eV,

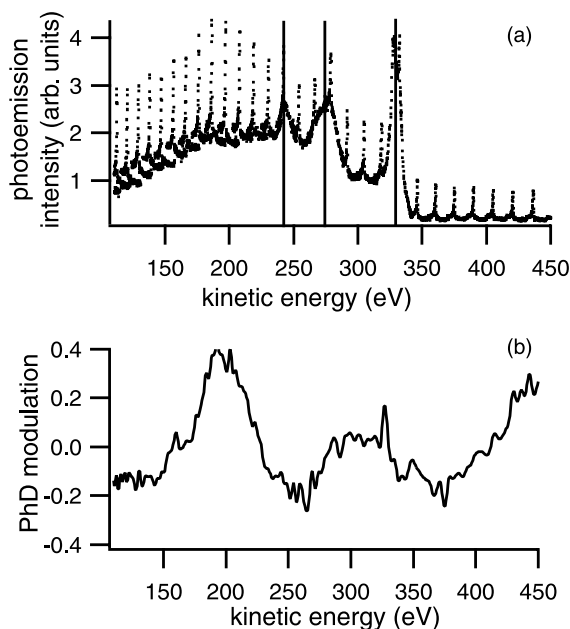


Fig. 1. (a) A superposition of a subset of the C 1s photoelectron EDCs measured in normal emission from the Pd(110)(2 × 1)-CO surface which are used to obtain the associated PhD modulation spectrum. Note the intense Pd Auger electron emission peaks marked with vertical lines around kinetic energies of 240, 270 and 325 eV in the background. (b) The PhD modulation spectrum extracted from the complete data set for this experimental geometry.

but also showing that the narrow C 1s peaks are very clearly resolved on this changing background. The intensity of the C 1s peak in each EDC was then determined by subtracting a background template obtained from the wings of the individual EDCs (cf. Fig. 1(a)) and integration, and the resulting intensity-energy spectra being normalised by a smooth spline through the integrated intensities representing the combination of intrinsic atomic cross-section variations and instrumental effects. The resulting photoelectron diffraction modulation functions (e.g. Fig. 1(b)) form the primary data set for the structure analysis. Measurements were made at a series of polar emission angles in 10–20° steps, mainly in the $\langle 110 \rangle$ azimuth but also in the $\langle 111 \rangle$, $\langle 112 \rangle$ and $\langle 100 \rangle$ azimuths. During the course of the characterisation of the CO-covered surface it was found that the C 1s spectrum changed with time, the intensity

being transferred to a second peak with a binding energy 1.8 eV lower. We attributed this to the effect of damage (mainly dissociation) induced by the incident soft X-radiation. In its standard operating conditions this beamline has a focussed spot size on the sample of only about 50 μm leading to a large enhancement of the flux density. In order to overcome the effects of this radiation-induced damage the beam was defocused and careful checks were conducted to ensure that no significant beam damage occurred during PhD data collection. However, the defocused beam did lead to a substantial deterioration of the signal-to-noise quality of the data. All PhD spectra were recorded at a sample temperature of approximately 150 K; the low temperature reduces the amplitude of thermal vibrations and hence leads to stronger PhD modulations. Low temperatures can also reduce radiation damage.

3. Results

The primary method of determining the surface structure from a PhD data set is to simulate these data, using multiple scattering calculations, for a series of trial structures, modifying and refining these until the best fit is obtained. Generally [32,35] our complete methodology comprises two steps; in the first of these a direct inversion of the experimental modulation spectra [36,37] is used to give an approximate ‘image’ of the backscatterer atoms which are near-neighbours to the emitter. In the present case a combination of factors, including the need for a particularly large data set of different azimuths for the twofold symmetric (110) surface and previously identified problems with the direct inversion of Pd backscattering data [38], meant that this first stage did not prove viable in the present case. Of course, our special interest here is in distinguishing two specific possible adsorption sites—atop and short bridge—so proper evaluation of these two structures is necessary whatever the outcome of the (approximate or indicative) direct data inversion approach might indicate.

Our multiple scattering modelling of the experimental data using a succession of trial structures

was performed using computational codes developed by Fritzsche, which are based on an expansion of the scattering processes into scattering paths [39,40]. The successive scattering events on a scattering path are treated within a Green's function formalism using a magnetic quantum number expansion for the free electron propagator [41]. In order to provide an objective measure of the quality of agreement between the simulated and experimental modulation functions we have previously defined a reliability-factor (*R*-factor) *R* [42], which is a normalised sum of the squares of the differences between experiment and theory at each data point. The normalisation is such that *R* equals zero for complete agreement between theory and experiment, unity for no correlation between theory and experiment and a value of two for anti-correlation. In order to optimise the efficiency of the search of structural multi-parameter space around trial models to find the structure corresponding to the best agreement we use an adapted Newton–Gauss-algorithm in the optimisation [39]. The precision of the final structural parameters, and the significance of changes in the *R*-factor between different structural models, are established using a variance in the minimum value of the *R*-factor, R_{\min} , defined in a similar fashion to that of the Pendry *R*-factor in LEED [43]. In particular, we take $\text{var}(R_{\min}) = R_{\min} \sqrt{(2/N)}$ where *N* is the number of independent pieces of structural information contained in the data as described by us in more detail elsewhere [44]. Any structure which is found to have an associated *R*-factor less than $(R_{\min} + \text{var}(R_{\min}))$ is regarded as acceptable. In order to improve both the precision and uniqueness of the final structure determination our methodology involves the simultaneous fitting of PhD spectra recorded in typically 5–10 different emission directions. Usually the choice of which spectra to include from a somewhat larger experimental data set is to concentrate on using spectra which show strong modulations because these should be the most reliable features in both the experimental data and the theoretical simulations. Of course, the absence of strong modulations in certain directions is itself important information, but because spectra with weak modulations are more dominated by noise, even good

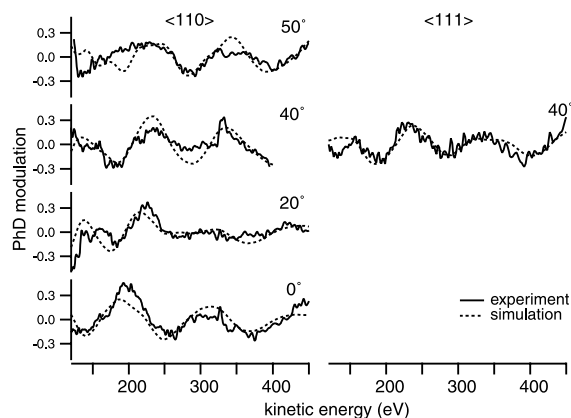


Fig. 2. Comparison of the experimental PhD modulation spectra (—) and the results of the simulations (---) for the best-fit adsorption structure as illustrated in Fig. 3 with the associated parameter values of Table 1.

overall fits will result in poor *R*-factor values for these spectra, and including many of these in the complete data set actually leads to a degradation of the precision of the structure determination. In the present case our final analysis was based on the five PhD spectra shown in Fig. 2. Other tests using larger data sets which included spectra with weaker modulations were found to converge on essentially the same structure, but the overall *R*-factor was worse. The need to use a defocused incident beam to avoid radiation damage appears to be the main origin of the relatively poor signal-to-noise ratio for many of these PhD modulation spectra.

Fig. 2 shows the comparison of these five PhD spectra with the results of the simulations for the best-fit structure based on short-bridge site occupation. The associated *R*-factor value was 0.31, whereas the best that could be achieved for the atop site was around 0.6 and further tests based on the long bridge site yielded even larger values. Clearly both of these alternative local sites can be rejected. The best-fit *R*-factor value of 0.31 represents a reasonable, but not exceptionally good, quality of fit; in very favourable circumstances we have obtained values below 0.1 for some systems, while values in the range 0.2–0.3 are quite common, but sometimes cannot be optimised much below about 0.4. The largest values usually correspond to situations in which the emitter atom is

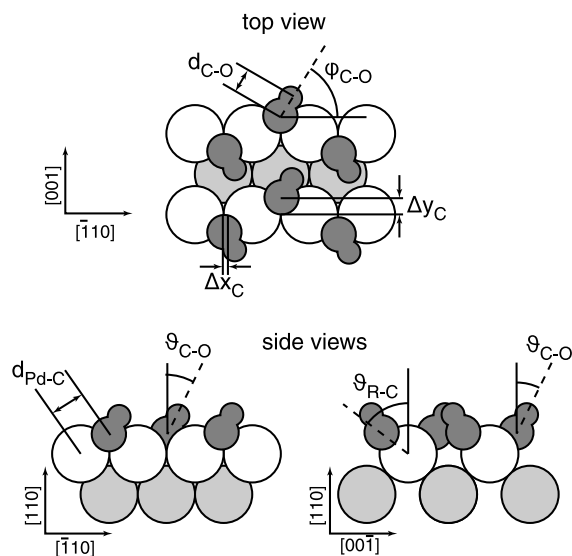


Fig. 3. Top and side views of a schematic diagram of the best-fit structural model based on (near-) bridge site occupation. The values of the structural parameters defined here are listed in Table 1. Note that θ_{C-O} is the polar tilt angle of the C–O axis relative to the surface normal and not simply the projection of this angle onto one of the principle azimuths as seen in the side views. ϕ_{C-O} defines the azimuthal plane of this tilt. θ_{R-C} is the polar tilt angle of the position of the C atom relative to the outermost Pd close-packed $\langle 110 \rangle$ row.

in a rather low symmetry site, when domain averaging suppresses the modulation amplitude of the PhD spectra; the present case is consistent with this trend, showing modulations of typically only about $\pm 20\%$. Fig. 3 shows schematically the actual best-fit structure and defines some of the structural parameters which were optimised. While the model is based on CO bonding in the short-bridge sites, a series of relaxations and distortions were allowed consistent with the (lower symmetry) $p1g1$ space group. In particular, the C–O axis of the molecule was allowed to tilt in any arbitrary direction (defined by a polar tilt angle θ_{C-O} and an azimuthal plane containing this tilt defined by ϕ_{C-O}), and the location of the C atom was not only allowed to be displaced in the $\langle 100 \rangle$ azimuth in which it remains in a bridging coordination, but could also be displaced to a lower symmetry site by displacement along the $\langle 110 \rangle$ azimuth. Other parameters varied were the height of the C atoms above the outermost Pd layer and the layer spacing

Table 1

Summary of the structural parameter values for the best-fit structure found in this study

Parameter	Value
d_{Pd-C}	$1.97 \pm 0.03 \text{ \AA}$
d_{C-O}	Fixed at 1.15 \AA
θ_{C-O}	$22 \pm 5^\circ$
ϕ_{C-O}	$60(+40/-20)^\circ$
Δz_{12}	$0.07 \pm 0.02 \text{ \AA}$
Δx_C	$0.06(+0.02/-0.07) \text{ \AA}$
Δy_C	$0.45 \pm 0.07 \text{ \AA}$
θ_{R-C}	$17 \pm 2^\circ$

Most of the parameter names are defined in Fig. 3. Δz_{12} is the expansion of the interlayer spacings of the first (outermost) and second Pd surface layers relative to the value for the ideally terminated bulk.

relaxation, Δz_{12} , of the outermost Pd layer. Possible lateral distortions of the outermost Pd layer atoms were also explored but found to have optimal values of zero. The best-fit structural parameter values are listed in Table 1. Note that in this final optimisation the C–O bond length was constrained to 1.15 \AA , essentially its gas-phase value. Because the O atom lies above the C atom, thus leading to quite small path-length differences in the single scattering from this atom, the effects of these scattering events on the PhD spectral modulations (dominated by backscattering) are not strong, and the precision with which the location of this atoms can be determined is poor. However, intramolecular multiple scattering events can be important, leading to a significantly greater influence of the O scattering. In the present case free optimisation favoured an unreasonably small value of 0.95 \AA for this bondlength. Optimisation of the primary parameters with the C–O bondlength fixed at a more reasonable value seemed more appropriate.

The process of optimising the fit between theory and experiment also involves the parameters defining the vibrational amplitudes of the scatterer atoms relative to the emitter; these parameters can be especially important to match the PhD modulation amplitudes. In order to take account of correlated vibrations of scatterer atoms which are nearest neighbours to the emitter, the emitter vibrations were set to zero and other mean-square vibrational amplitudes (of the nearest neighbour Pd atoms, the remainder of the Pd atoms, and the

Table 2

Comparison of the structural parameter values obtained in several studies of the Pd(110)(2 × 1)-CO surface phase, all corresponding to the (off-) short-bridge adsorption site

	$d_{\text{Pd-C}}$ (Å)	$\vartheta_{\text{R-C}}$ (°)	$d_{\text{C-O}}$ (Å)	$\vartheta_{\text{C-O}}$ (°)
This study	1.97 ± 0.03	17 ± 2	1.15 (fixed)	22 ± 5
XPD—Refs. [24,25]	1.84 ± 0.14	6 ± 6	1.15 (fixed)	24 ± 3
Theory—Ref. [23]	2.10	22	—	20
Theory—Ref. [22]	2.01	24.9	1.16	23.6
Theory—Ref. [21]	1.93	—	1.19	—
Theory—LDA—Ref. [19]	2.05	11.9	1.15	12.4
Theory—GGA—Ref. [19]	2.08	15.7	1.15	13.5

The original LEED results, for which the (off-) atop site was found, are not included.

O atoms) relative to the emitter were optimised. Estimating the true bulk vibrational amplitudes from the known Debye temperature for Pd one can then interpret the optimised relative vibrations in terms of absolute amplitudes. The resulting values indicate strong correlation in the nearest-neighbour vibrations and a true C mean-square vibrational amplitude of 0.02 Å^2 . However, because the PhD modulations are dominated by the scattering from the correlated nearest neighbour Pd atoms, the sensitivity of the results to the relative vibrational amplitudes of the sub-surface Pd atoms is very low, and essentially any value for the true C vibrational amplitude (between zero and infinity) falls within the variance.

Table 2 compares the values of optimised (static) structural parameters with the results of the various theoretical total energy calculations and the one experimental structure determination (using XPD) which concluded that the CO adsorbs in bridge sites. The quantitative LEED study is not included because this concluded that the local adsorption site was atop. Why this investigation should lead to an adsorption site which now must be regarded as incorrect is unclear, but it is notable that most of the original authors have been involved in the more recent contrasting density-functional theory calculations, suggesting that these authors also no longer accept this experimental result. Table 2 shows clear overall agreement in the main conclusions regarding the structure, although there are clearly significant variations in the values of the Pd–C nearest neighbour distance, the C–O tilt angle and the shift of the C atom along $\langle 100 \rangle$ from the symmetric bridge site, reflected in the rotation angle $\vartheta_{\text{R-C}}$,

between the different theoretical calculations. In the case of the C–O tilt angle our experimental value is in excellent agreement with the XPD study and the more recent theoretical calculations. The value of the angle $\vartheta_{\text{R-C}}$ varies rather more, but the anomalous value seems to be that of the XPD experiments. There is also a surprisingly large scatter of Pd–C nearest neighbour distances in the different theoretical studies from 1.90 to 2.08 Å, although the largest values also correspond to the earliest calculations. Our own value of $1.97 \pm 0.03 \text{ Å}$ is in the middle of this theoretical range and is formally consistent with, but much more precise than, the value obtained in the XPD investigation.

One key question we have not addressed so far is the symmetry of the surface structure. The missing LEED beams imply either the p1g1 or p2mg space groups, and the ESDIAD and ARUPS studies favoured the more symmetric p2mg structure, although some distortions which would lower the symmetry to p1g1 cannot be excluded by either of these investigations, despite statements to the contrary. By reference to Fig. 3 we see that the p2mg symmetry arises if $\Delta x_{\text{C}} = 0$ and $\phi_{\text{C-O}} = 90^\circ$. Our best-fit values of these parameters (Table 1) differ from these requirements, but not by a formally significant amount in that these more symmetric values fall within our estimated precision limits. Our results thus are consistent with p2mg symmetry, but formally favour p1g1.

4. Conclusions

The results of our new PhD investigation of the Pd(110)(2 × 1)-CO resolve a longstanding

controversy concerning this system. While the only experimental quantitative structure determinations of other fcc(110)(2 × 1)-CO (1 ML) phases (on Ni(110) [30,31] and Rh(110) [45]) both show occupation of tilted bridge sites, and this site is favoured by total energy calculations and an XPD study on Pd(110), the only full quantitative structure determination of this surface by LEED concluded that the adsorption site was near atop. Our results clearly exclude this possibility, and show that tilted bridge sites are also occupied on this surface. The pattern of the local geometry in these structures therefore seems consistent (and unlike the case of c(4 × 2)-CO phases on Ni(111), Pd(111) and Pt(111)). Our results also provide rather precise values for several of the key structural parameters, notably the Pd–C nearest-neighbour distance, for which there is a surprisingly large variation in the various density-functional theory calculations which have been performed on this system. In the past there has been some debate as to whether the structure of these CO phases on fcc(110) surface have p1g1 or p2mg symmetry. Quite a number of investigations indicate either that the higher symmetry is present or that it is broken only by small (but unquantified) distortions, but the LEED structural studies on the Ni(110) and Rh(110) surfaces specifically assumed that the symmetry is p2mg [30,31,45]. In our investigation we have not imposed this constraint, and find a best-fit structure which has p1g1 symmetry, but the limits of precision include the more symmetric p2mg structure.

In the original LEED analysis of this surface the issue of the validity of CO site identification through vibrational spectral fingerprinting of the C–O stretch was raised. The value of this frequency is very close to 2000 cm⁻¹ for the (2 × 1)-CO phase on both Pd(110) and Ni(110), and the fact that the LEED analysis found (off-) atop adsorption on Pd(110) whereas the (off-) bridge site had been confirmed on Ni(110) was cited as evidence of the unreliability of this fingerprinting method. It is now clear that *both* surfaces involve (off-) bridge sites, so this argument is no longer valid. The actual value of 2000 cm⁻¹ lies at the boundary of the ranges usually associated with bridge and atop bonding, so this value alone is not

really a reliable basis for site assignment, although the fact that the frequency is lower at lower coverages suggests its high value arises from dynamic dipole coupling in the high coverage (2 × 1) phase. On this basis, the vibrational spectroscopy interpretation of bridge site occupation has proved to be essentially correct.

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References

- [1] N. Sheppard, N.T. Nguyen, *Adv. IR Raman Spectrosc.* 5 (1978) 67.
- [2] L. Becker, S. Aminpirooz, B. Hillert, M. Pedio, J. Haase, D.L. Adams, *Phys. Rev. B* 47 (1993) 9710.
- [3] K.-M. Schindler, Ph. Hofmann, K.-U. Weiss, R. Dippel, P. Gardner, V. Fritzsche, A.M. Bradshaw, D.P. Woodruff, M.E. Davila, M.C. Asensio, J.C. Conesa, A.R. Gonzalez-Elipe, *J. Electron Spectrosc. Rel. Phenom.* 64/65 (1993) 75.
- [4] M.E. Davila, M.C. Asensio, D.P. Woodruff, K.-M. Schindler, Ph. Hofmann, K.-U. Weiss, R. Dippel, P. Gardner, V. Fritzsche, A.M. Bradshaw, J.C. Conesa, A.R. González-Elipe, *Surf. Sci.* 311 (1994) 337.
- [5] L.D. Mapledoram, M.P. Bessent, A.D. Wander, D.A. King, *Chem. Phys. Lett.* 228 (1994) 527.
- [6] V. Fernandez, T. Giessel, O. Schaff, K.-M. Schindler, A. Theobald, C.J. Hirschmugl, S. Bao, A.M. Bradshaw, C. Baddeley, A.F. Lee, R.M. Lambert, D.P. Woodruff, V. Fritzsche, *Z. Phys. Chem.* 198 (1997) 73.
- [7] T. Gießel, O. Schaff, C.J. Hirschmugl, V. Fernandez, K.-M. Schindler, A. Theobald, S. Bao, R. Lindsay, W. Berndt, A.M. Bradshaw, C. Baddeley, A.F. Lee, R.M. Lambert, D.P. Woodruff, *Surf. Sci.* 406 (1998) 90.
- [8] P.R. Watson, M.A. Van Hove, K. Hermann, NIST Surface Structure Database Ver. 4, NIST Standard Reference Data Program, Gaithersburg, MD, 2001.
- [9] R.M. Lambert, *Surf. Sci.* 49 (1975) 325.
- [10] P. Hofmann, S.R. Bare, N.V. Richardson, D.A. King, *Surf. Sci.* 133 (1983) L459.
- [11] W. Riedl, D. Menzel, *Surf. Sci.* 163 (1985) 39.

- [12] H. Kühlenbeck, M. Neumann, H.-J. Freund, *Surf. Sci.* 173 (1986) 194.
- [13] D.A. Wesner, F.P. Coenen, H.P. Bonzel, *Surf. Sci.* 199 (1988) L419.
- [14] D.F. Ogletree, M.A. Van Hove, G.A. Somorjai, *Surf. Sci.* 173 (1986) 351.
- [15] R. Raval, S. Haq, G. Blyholder, D.A. King, *J. Electron Spectrosc. Rel. Phenom.* 54/55 (1990) 629.
- [16] R. Raval, S. Haq, M.A. Harrison, G. Blyholder, D.A. King, *Chem. Phys. Lett.* 167 (1990) 391.
- [17] P. Hu, L.M. de la Garza, R. Raval, D.A. King, *Surf. Sci.* 249 (1991) 1.
- [18] A. Wander, P. Hu, D.A. King, *Chem. Phys. Lett.* 201 (1993) 393.
- [19] P. Hu, D.A. King, S. Crampin, M.-H. Lee, M.C. Payne, *Chem. Phys. Lett.* 230 (1994) 501.
- [20] P. Hu, D.A. King, M.-H. Lee, M.C. Payne, *Chem. Phys. Lett.* 246 (1995) 73.
- [21] L. Pedocchi, M.R. Ji, S. Lizzit, G. Comelli, G. Rovida, *J. Electron Spectrosc. Rel. Phenom.* 76 (1995) 383.
- [22] R. Ramprasad, K.M. Glassford, J.B. Adams, R.I. Masel, *Surf. Sci.* 360 (1996) 31.
- [23] P. Hu, D.A. King, S. Crampin, M.-H. Lee, M.C. Payne, *J. Chem. Phys.* 107 (1997) 8103.
- [24] A. Locatelli, B. Brena, S. Lizzit, G. Comelli, G. Cautero, G. Paolucci, R. Rosei, *Phys. Rev. Lett.* 73 (1994) 90.
- [25] A. Locatelli, B. Brena, G. Comelli, S. Lizzit, G. Paolucci, R. Rosei, *Phys. Rev. B* 54 (1996) 2839.
- [26] R.P. Eischens, W.A. Pliskin, *Adv. Catal.* 10 (1958) 1.
- [27] M.A. Chesters, G.S. McDougall, M.E. Pemble, N. Sheppard, *Surf. Sci.* 164 (1985) 425.
- [28] B. Voigtländer, D. Bruchmann, S. Lehwald, H. Ibach, *Surf. Sci.* 225 (1990) 151.
- [29] S. Haq, J.G. Love, D.A. King, *Surf. Sci.* 275 (1992) 170.
- [30] D.J. Hannaman, M.A. Passler, *Surf. Sci.* 203 (1988) 449.
- [31] C. Zhao, M.A. Passler, *Surf. Sci.* 320 (1994) 1.
- [32] D.P. Woodruff, A.M. Bradshaw, *Rep. Prog. Phys.* 57 (1994) 1029.
- [33] J.D. Denlinger, E. Rotenberg, T. Warwick, G. Visser, J. Nordgren, J.-H. Guo, P. Skytt, S.D. Kevan, K.S. McCutcheon, D. Shuh, J. Bucher, N. Edelstein, J.G. Tobin, B.P. Tonner, *Rev. Sci. Instrum.* 66 (1995) 1342.
- [34] T. Warwick, P. Heimann, D. Mossessian, W. McKinney, H. Padmore, *Rev. Sci. Instrum.* 66 (1995) 2037.
- [35] D.P. Woodruff, R. Davis, N.A. Booth, A.M. Bradshaw, C.J. Hirschmugl, K.-M. Schindler, O. Schaff, V. Fernandez, A. Theobald, Ph. Hofmann, V. Fritzsche, *Surf. Sci.* 357/358 (1996) 19.
- [36] Ph. Hofmann, K.-M. Schindler, *Phys. Rev. B* 47 (1993) 13941.
- [37] Ph. Hofmann, K.-M. Schindler, S. Bao, A.M. Bradshaw, D.P. Woodruff, *Nature* 368 (1994) 131.
- [38] D.P. Woodruff, P. Baumgärtel, J.T. Hoeft, M. Kittel, M. Polcik, *J. Phys.: Condens. Matter* 13 (2001) 10625.
- [39] V. Fritzsche, *Surf. Sci.* 213 (1989) 648.
- [40] V. Fritzsche, *J. Phys.: Condens. Matter* 2 (1990) 1413.
- [41] V. Fritzsche, *Surf. Sci.* 265 (1992) 187.
- [42] R. Dippel, K.-U. Weiss, K.-M. Schindler, P. Gardner, V. Fritzsche, A.M. Bradshaw, M.C. Asensio, X.M. Hu, D.P. Woodruff, A.R. González-Elipe, *Chem. Phys. Lett.* 199 (1992) 625.
- [43] J.B. Pendry, *J. Phys. C: Solid State Phys.* 13 (1980) 937.
- [44] N.A. Booth, R. Davis, R. Toomes, D.P. Woodruff, C. Hirschmugl, K.-M. Schindler, O. Schaff, V. Fernandez, A. Theobald, Ph. Hofmann, R. Lindsay, T. Giessel, P. Baumgärtel, A.M. Bradshaw, *Surf. Sci.* 387 (1997) 152.
- [45] J.D. Batteas, A. Barbieri, E.K. Starkey, M.A. Van Hove, G.A. Somorjai, *Surf. Sci.* 313 (1994) 341.